

# A STUDY OF CHEMICAL DEHYDRATION OF COALS AND ITS EFFECT ON COAL LIQUEFACTION YIELDS

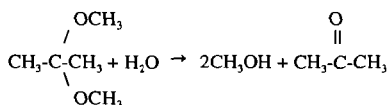
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## INTRODUCTION

Although great strides have been made in developing the technology of coal liquefaction processes in recent years, many unsolved problems still remain before a viable and economical process can be achieved. The technological problems that still exist can be solved through a more fundamental understanding of the chemistry associated with each stage of the coal liquefaction process, starting with any pretreatment steps that may be carried out on the coal itself. One pretreatment process which can improve the economics of coal liquefaction is coal drying, particularly for the lower rank coals. However, there is also considerable evidence to show that drying has a detrimental effect on the liquefaction behavior of coals.<sup>1-3</sup> The problem that needs to be solved is that of economically drying coal without adversely affecting its liquefaction reactivity. Only recently have there been any systematic studies of the methods of coal drying on coal structure and the role water plays in enhancing or lessening coal reactivity toward liquefaction.<sup>4-5</sup> Thermal methods of drying can alter the physical structure of coal as well as promote undesirable chemical reactions. Low-temperature drying of coal, on the other hand, should preserve the structural integrity, reduce retrograde reactions, reduce thermal degradation, and provide information on nonbonded, chemisorbed, and physisorbed water. Chemical drying of coals is a relatively unexplored technique for removing water at low temperature.

A common chemical dehydrating agent is 2,2-dimethoxypropane. This agent has been used in inorganic chemistry to remove water of hydration in inorganic compounds<sup>6</sup> and in biological sciences for drying tissues for microscopic examination.<sup>7,8</sup> The reaction of 2,2-dimethoxypropane (DMP) with water is shown in scheme I.<sup>9</sup>



Scheme I

This reaction is rapid and endothermic. The reaction products, methanol and acetone, are removed by vacuum at ambient temperature. Removing water by chemical means rather than by physically forcing exchange by mass action preserves the ultrastructural integrity of the coal cellular components. The use of the dehydration agent, 2,2-dimethoxypropane, in this study to dry coals is a novel and innovative approach to the understanding of the role of water in coal chemistry.<sup>10</sup>

## EXPERIMENTAL

Of the six coals used in this study four were obtained from the Pennsylvania State University, Coal Research Section, and two were obtained from the Powder River Basin in Wyoming. The coals selected for study consisted of a lignite, three subbituminous, and two bituminous coals. Bulk samples of these coals were premoisturized in a constant humidity chamber at 30°C for 24 hours. The moisture content determined thermally was used as the reference moisture content for the coals.

Coal samples were dried with DMP before coal liquefaction. Depending upon the amount of moisture in the coal, between 22 and 72 grams of DMP, and between 6 and 25 mL of 0.2 N methanesulfonic acid in methanol were added to a 20 g sample of coal. The acid-methanol solution was added to the sample, followed by DMP. The contents of the flask were shaken to ensure good mixing and contact. The mixture was allowed to stand for 24 hrs. The liquid was then decanted and a vacuum was applied to remove the remaining liquid (excess DMP and methanol).

A modified "Borgialli" microreactor<sup>1</sup> was used for the liquefaction of the coals. The key features of this reactor system are: rapid heating through submergence in a fluidized sandbath,

pneumatic control of the extent of autoclave submergence, and continuous stirring using a magnetically-coupled stirrer. The gases produced during the coal liquefaction process were collected in a gas bomb and analyzed using an HP 5890 Series II GC fitted with both FID and TCD detectors. A 6 ft, Porapak N, packed column was used to separate the gases. Upon completion of the coal liquefaction experiment, the reactor was opened, and the soluble coal products and residue were rinsed using  $\text{CH}_2\text{Cl}_2$  into a Soxhlet thimble. Soxhlet extraction was carried out for 30 hr at the refluxing temperature of  $\text{CH}_2\text{Cl}_2$ . The solid residue in the Soxhlet thimble and the thimble were placed into a furnace set at  $\sim 100^\circ\text{C}$  for 20 hrs to remove solvent. The coal residues were characterized using solid-state carbon-13 NMR. Solvent swelling of the coal samples was conducted using the procedure described by Green et al.<sup>12</sup>

Solid-state  $^{13}\text{C}$  NMR measurements were made using a Chemagnetics 100/200 solids NMR spectrometer. Carbon aromaticity measurements were made at 25 MHz using the technique of cross polarization (CP) with magic-angle spinning (MAS) and high-power decoupling. These measurements were made using either a large-volume sample spinner (2.1 mL) at a spinning rate of  $\sim 3.8$  kHz or a 7.5 mm (OD) sample spinner at a spinning rate of 4.5 kHz. Between 3,600 and 7,200 transients were recorded. Other instrument parameters were a pulse delay of 1 s, a contact time of 1 ms, a 6.2  $\mu\text{s}$  (large volume spinner) and 5  $\mu\text{s}$  (7.5 mm spinner) pulse widths, a sweep width of 16 kHz, and 1 K data acquisition points. A 25 or 50 Hz exponential multiplier was applied to the free induction decay of each  $^{13}\text{C}$  spectrum before integration.

A TA instruments 2910 Differential Scanning Calorimeter (DSC) with a liquid nitrogen cooling accessory (LNCA) was used in this study to determine the amount of solvents retained by the coals after chemical dehydration.

## RESULTS AND DISCUSSION

### A. Effects of Chemical Drying Process on the Structure of Coals

1. Chemical Drying Kinetics. A typical plot of the weight percent of moisture removed from the coal samples as a function of time in which the coals are in contact with DMP is shown in Figure 1. In all cases a significant amount of moisture is removed in the first minute of the reaction. The initial reaction is DMP with physisorbed surface water and free water in the pores near the surface of the coal. Removal of the remaining moisture requires longer times and is due to diffusion control of DMP into the smaller pores within the coals.

The chemical drying data after the fast initial reaction were fit to  $1^{\text{st}}$ - and  $n^{\text{th}}$ -order kinetic equations. The kinetic parameters are listed in Table I. The initial concentration,  $C_i$ , shown in the table is defined as the percent of physisorbed and free surface moisture removed from the coal during the initial reaction of water and DMP. This reaction occurs almost instantaneously. The value of  $C_i$  for both the first order and  $n^{\text{th}}$  order reactions increases with decreasing coal rank. That is, the higher rank coals are generally less porous and have less adsorbed water than the lower rank coals. For Wyoming Black Thunder coal, the  $C_i$  value is higher than expected and may be due to the smaller mesh size of the coal sample compared to the other coals.

The percent of moisture in coal at  $t = \infty$ , but not including the water removed during the initial reaction, is  $M_{\infty}$ . The sum of  $C_i$  and  $M_{\infty}$  gives the total amount of water in each coal sample. These values exceed their respective thermal moisture values especially for the low rank coals.

Table I also lists the percent of readily accessible water (sorbed surface water) for each coal. As shown in the table, the percent of loosely bound surface water increases with decreasing rank of the coal. Based on a first-order kinetics analysis of the data, the Utah Blind Canyon coals have the lowest amount of surface water (12.2%) whereas the Texas Bottom coal and North Dakota Beulah lignite have almost two-thirds of the total water near or on the surface and readily accessible to react with DMP (62.0 and 64.4%, respectively). Figure 2 is a plot of the percent of surface water as a function of the rank of coal based upon the fixed carbon content. Wroblewski and Verkade<sup>13</sup> also measured the different types of moisture in coals using several extraction solvents and measuring the moisture content in the extracts over an eight hour period. These authors found that of the total moisture content, the higher rank coals have less surface water than the lower rank coals in qualitative agreement with the results shown in Figure 2.

2.  $^{13}\text{C}$  NMR. The  $^{13}\text{C}$  CP/MAS NMR spectra of the premoisturized and chemically dried Wyoming Eagle Butte coal is shown in Figures 3a and 3b. There appears to be enhanced resolution in the aromatic (100-210 ppm) and aliphatic (0-80 ppm) carbon regions of the spectra. Decarboxylation in the aromatic region is not apparent. The enhanced resolution in the aliphatic carbon region may be due to (1) the tightly bound residual solvents and/or reaction products such as methanol that had replaced the water and (2) increased mobility of some coal

components because of less secondary interactions resulting from the loss of the strongly hydrogen bonded water. Only slight changes (within experimental error) are noted for the carbon aromaticity values for chemical dried coals relative to the premoisturized coals. Thus, chemical drying had little or no effect on the organic composition of the coals. However, the extent of physical association of the coal molecule had been altered due to the loss of water which may have affected the overall coal structure.<sup>13</sup>

3. Differential Scanning Calorimetry of Coals. The solid-state <sup>13</sup>C NMR spectra of chemically dried coals showed additional carbon resonances and/or increased resolution in the aliphatic carbon region. The changes in the spectra were assumed to be due to sorbed solvents and/or reaction products occupying surface and pore sites previously held by water. DSC was used to identify and quantify the sorbed species for the chemically dehydrated coals. For the chemically dried coal samples, losses could conceivably be from vaporization of methanol, acetone, water, or a combination of the three. Fortunately, the heats of vaporization of the three materials are significantly different, and a tentative identification of the material is possible if it is assumed that only one material is lost. For all chemically-dried coals, except Utah Blind Canyon, the material lost appears to be methanol with an average heat of vaporization of 1136 J/g and a standard deviation of 100 J/g. The literature value is 1224.5 J/g. The measured heat of vaporization for the Utah coal is close to the literature value for acetone, however, the weight loss for this material and the transition energy are small decreasing the accuracy of both measurements and placing the identification of the material in some doubt.

4. Swelling Index. The swelling index profile parameter<sup>14</sup> of the chemically dehydrated coals is given in Table II. This parameter for Illinois # 6 and Texas Bottom coals shows a small decrease relative to the swelling index parameter of the premoisturized coals, whereas, Utah Blind Canyon, Wyoming Eagle Butte, Wyoming Black Thunder, and North Dakota Beulah coals show a significant increase. The data show that only a small increase or no change in the cross-linking internal structure for the Illinois # 6 and Texas Bottom coals had occurred as a result of chemical dehydration. However, a significant decrease in the cross-linking structure ( $1 - X > 1$ ) is observed for the other four coals. The incorporation of CH<sub>3</sub>OH at the sites previously occupied by water molecules would decrease the extent of relatively strong secondary interactions involving ionized groups, charge-transfer complexes and  $\pi$ - $\pi$  interactions as well as hydrogen bonding and weak van der Waal's forces.<sup>15</sup> A decrease in these interactions, in effect, would reduce the cross-linking due to physical association relative to the premoisturized coal.

#### B. Effects of Chemical Drying Process on the Reactivity of Coals

Table III gives the results of the coal liquefaction of the six coals that were chemically dried. The table contains data on the percentage of gas, liquid, and residue produced, and the percent conversion. Relative to the premoisturized coals (0% water removed), drying the coals by chemical dehydration, in general, increased the conversion yield. Utah Blind Canyon and North Dakota Beulah coals showed little or no change in the conversion yield.

Except for the chemically dried coals, the conversions are generally less for coals dried by thermal methods.<sup>14,16</sup> The reason for the differences in liquefaction behavior of the chemically dried and the thermally dried coals appears to be due to the retention of the reaction products and solvents by the chemically dried coals. DSC has shown that some of the methanol was incorporated into the coal pore structure in place of the water, thus possibly preventing collapse of the pore structure during the dehydration reaction. This would allow for greater diffusion of tetralin during liquefaction and hence greater conversion. Relative to the premoisturized coal, all chemically dried coals show an increase in the coal liquid yield. This increase may also be the result of replacement of water by CH<sub>3</sub>OH in the internal structure of coal thereby reducing the strong hydrogen bonding effect caused by water. In general, there is increase in total percent of gas produced with decreasing rank of the premoisturized coals (Utah to North Dakota). Both the Utah and North Dakota coals show a significant decrease in gas produced when completely dried. The total amount of gases produced from the other four dried coals is essentially the same as their corresponding premoisturized coals. The amount of coal residue produced during liquefaction of the premoisturized coals (Table III) decreases with the increase in the moisture content of the coal (decrease in coal rank).

The <sup>13</sup>C CP/MAS NMR spectra of the coal liquefaction CH<sub>2</sub>Cl<sub>2</sub> extracted residues from the premoisturized and chemically dried Texas Bottom coals are shown in Figures 4a and 4b. When compared to the starting coal spectrum, the NMR spectra of the residues show a significant reduction in the aliphatic component relative to the aromatic component. There is also a shift in the resonance position from ~ 30 ppm to ~ 20 ppm for the aliphatic carbons. The residual

aliphatic component at ~ 20 ppm could be due to methyl groups attached to aromatic rings that would not be cleaved during liquefaction at 425°C.

The significant difference in the residue NMR spectra of the Texas Bottom coal as well as for the other five coals is the enhanced resolution of the aliphatic carbons for the coals dried via chemical dehydration. This enhanced resolution of the aliphatic carbons in the  $^{13}\text{C}$  NMR spectra was also noted in the NMR spectra of the chemically dried coals before liquefaction. However, it is unlikely that the carbon resonances observed are due to solvent and reaction products of the chemical drying technique unless the methanol is strongly adsorbed even at the liquefaction temperature of 425°C. It may be that the methanol solvent removed some of the soluble aliphatic carbon substituents (decreasing the chemical shift dispersion) and, thus, in effect giving higher resolution of the remaining carbons types.

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Table I. Kinetic Parameters for the Chemical Dehydration of Coals

Coal		Kinetic Parameters					
		Order n	Rate Constant k, hr <sup>-1</sup>	Initial Concen- tration of water, C <sub>i</sub> (%)	Final Concen- tration of water, M <sub>∞</sub> (%)	Total Concen- tration of Water (%) C <sub>i</sub> + M <sub>∞</sub>	Percent of Surface Water C <sub>i</sub> /(C <sub>i</sub> +M <sub>∞</sub> )
Utah Blind Canyon	1 <sup>st</sup> order	1	3.59 x 10 <sup>-3</sup>	0.89	6.41	7.3	12.2
	n <sup>th</sup> order	0.893	4.15 x 10 <sup>-3</sup>	0.94	6.31	7.3	13.0
Illinois # 6	1 <sup>st</sup> order	1	1.93 x 10 <sup>-2</sup>	4.6	6.5	11.1	41.4
	n <sup>th</sup> order	1.07	2.49 x 10 <sup>-2</sup>	4.5	6.6	11.1	40.5
Wyoming Eagle Butte	1 <sup>st</sup> order	1	2.17 x 10 <sup>-3</sup>	12.5	11.5	24.0	52.1
	n <sup>th</sup> order	3.62	0.157	11.2	18.8	30.0	37.3
Wyoming Black Thunder	1 <sup>st</sup> order	1	1.85 x 10 <sup>-3</sup>	19.9	2.2	22.1	90.1
	n <sup>th</sup> order	0.943	1.62 x 10 <sup>-2</sup>	15.3	7.1	22.4	68.3
Texas Bottom	1 <sup>st</sup> order	1	8.39 x 10 <sup>-3</sup>	18.4	11.3	29.7	62.0
	n <sup>th</sup> order	5.61	12.8	13.0	23.6	36.6	35.5
North Dakota Beulah	1 <sup>st</sup> order	1	1.11 x 10 <sup>-3</sup>	24.6	13.6	38.2	64.4
	n <sup>th</sup> order	1.32	4.29 x 10 <sup>-4</sup>	24.6	15.4	40.0	63.1

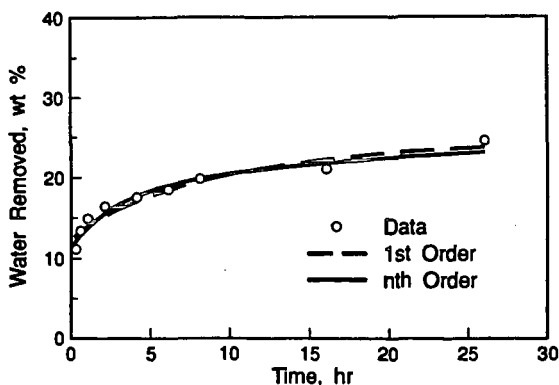
**Table II. Solvent Swelling Profile Parameter<sup>a</sup> of Premoisturized Coals and Chemically Dried Coals**

Coal	Swelling Parameter (1-X) using 1,4-Dioxane	
	Premoisturized Coal	Chemically Dried
Utah Blind Canyon	1.0	1.61
Illinois # 6	1.0	0.95
Wyoming Eagle Butte	1.0	1.50
Wyoming Black Thunder	1.0	1.51
Texas Bottom	1.0	0.84
North Dakota Beulah	1.0	1.10

<sup>a</sup>  $X = (Q_{\text{coal}} - Q_{\text{v,dry}}) / (Q_{\text{coal}} - 1)$  where X = swelling index;  $Q_{\text{coal}}$  = swelling ratio of the premoisturized coal; and  $Q_{\text{v,dry}}$  = swelling ratio of the dried coal.

**Table III. Percentages of Gas, Liquid, Residue, and Conversion from the Liquefaction of Coals Dried using the Chemical Dehydration Method**

Coal	Percent Water Removed	Percent Gas	Percent Liquid	Percent Residue	Percent Conversion
Utah Blind Canyon	0	9.1	61.0	30.0	70
	100	4.0	63.7	32.3	67.7
Illinois # 6	0	3.4	64.3	32.4	67.6
	100	5.3	74.4	20.2	79.8
Wyoming Eagle Butte	0	10.9	62.3	26.8	73.2
	100	10.0	75.1	14.9	85.1
Wyoming Black Thunder	0	11.4	67.6	21.0	79.0
	100	9.7	72.4	17.9	82.1
Texas Bottom	0	12.4	70.0	17.6	82.4
	100	10.2	77.2	12.6	87.4
North Dakota Beulah	0	35.6	38.8	25.6	74.4
	100	12.1	62.1	25.8	74.2



**Figure 1. Weight Percent of Water Removed by DMP in Wyoming Eagle Butte Coal as a Function of Time**

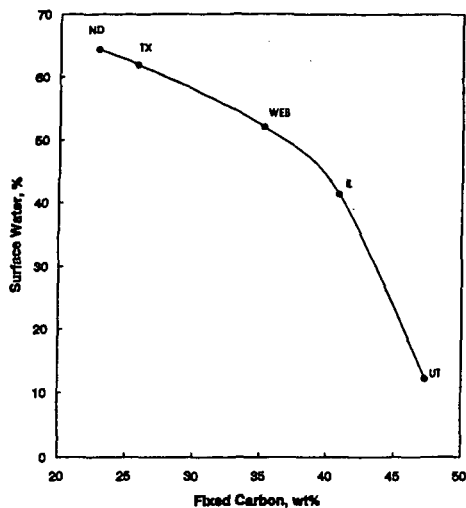


Figure 2. A Plot of the Percent Surface Water for Coals as a Function of the Coal Rank (wt % of fix carbon)

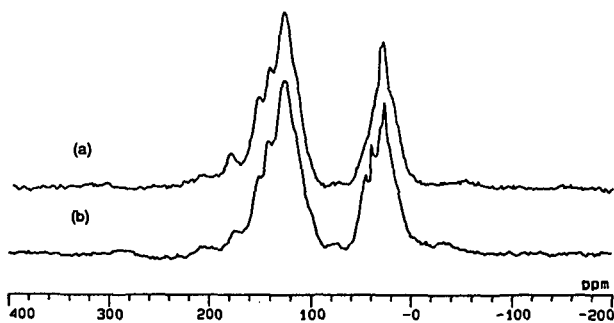


Figure 3. Carbon-13 NMR Spectra of Wyoming Eagle Butte Coal: (a) Premoisturized Coal and (b) Chemically Dried Coal

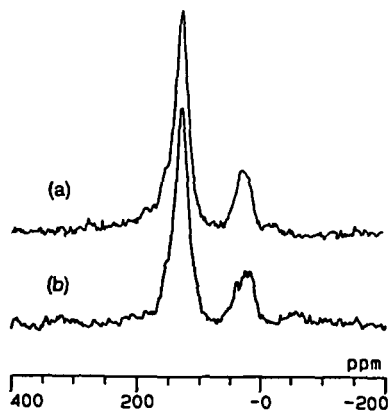


Figure 4. Carbon-13 NMR Spectra of Texas Bottom Coal Residues from Coal Liquefaction of (a) Premoisturized Coal and (b) Chemically Dried Coal